REACTION RATES OF A FEW BENZYL TYPE RADICALS WITH O_2, NO AND NO_2

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Introduction

Benzyl type radicals are important conjugated intermediates in the chemical mechanisms describing the oxidation of alkylbenzenes in reactive systems. In the atmosphere, they are formed during the first step (by OH abstraction) of the tropospheric oxidation of alkylbenzene derivatives (toluene, xylenes, trimethylbenzenes) : final oxidation are formed by subsequent competing reactions of the benzyl type radicals with O_2, NO and NO_2 (1) (2). In high temperature reactive systems, they can also play a role as intermediates in the mechanism of soot formation (3) (4) (5) (6). At last, with the allyl radical, the benzyl radical is a reference conjugated radical. With an absolute technique, the discharge flow/Laser Induced Fluorescence technique, we have measured the room temperature rate constants with O_2, NO and NO_2 of the following benzyl type radicals : m-fluorobenzyl, p-fluorobenzyl, o-methylbenzyl, m-methylbenzyl. Also, the rate constant with O_2 of the p-fluorobenzyl radical has been measured in the temperature range 297-433 K.

Experimental

A schematics of the experimental set up is presented figure 1. The radicals are formed by chlorine atom reaction with the parent molecule as a precursor. Chlorine atoms are prepared in the upstream part of the flow tube by the fast reaction of transfer (7) :

$$F + Cl_2 \longrightarrow FCl + Cl \qquad k = 1.6 \times 10^{-11}\ cm^3\ molec^{-1}\ s^{-1}$$

with F atoms first produced by a microwave discharge in F_2/He or CF_4/He. This method (chlorine abstraction) has been preferred to the more direct fluorine abstraction because (i) a significant fraction of fluorine atoms exhibit an addition on the aromatic ring (8) (9) (ii) chlorine abstraction is a very fast reaction ($k = 6 \times 10^{-10}$ cm^3 $molec^{-1}$ s^{-1} (10)). The precursor and the reactant (O_2, NO or NO_2) are then successively added via a double movable injector. The benzyl type radicals are probed by Laser Induced Fluorescence via their visible absorption bands ($\lambda \sim 460$ nm) which have been characterized in gas phase either as absorption bands (13) or as fluorescence excitation bands (11) (12). The exciting wavelength ($\lambda \sim 460$ nm) is generated by a dye laser (Rhodamine 590) pumped by a Yag laser (both Quantel) and further blueshifted (generation of the first Anti-Stokes harmonics) via a Raman cell (14). The fluorescent light is filtered by an interference filter ($\lambda = (500 \pm 20)$ nm) and averaged by a boxcar (PAR 162/165).

For the room temperature measurements, both the flow tube and the injector are covered with a halocarbon, wax whereas for variable temperature measurements, all flow surfaces are simply washed with HF. Most experiments have been performed at a pressure of 1 torr with Helium as diluent gas. O_2 (Alphagaz N45, 99.995%) is used as received. NO_2 is purified as follows : to oxidize the other nitrogen oxides usually present

in NO_2 (bluish color at 77 K), liquid NO_2 is first placed under ultrapure oxygen during $\sim$ 24 hours and then submitted to extensive degassing at 77 K. Traces of NO_2 present in NO (Alphagaz N20, 99%) have been eliminated by flowing NO through a combination of charcoal filter and a filter packed with $FeSO_4$, $7H_2O$ (15).

Results and discussion

1) Rate constants of a few benzyl type radicals with O_2, NO and NO_2.

A few typical curves observed with the p-fluorobenzyl radical as an example are presented figure 2 : fig 2a represents a few logarithmic decay plots of radical concentration versus reaction distance ; fig 2b represents all the pseudo-first-order constants versus the reactant concentration. Our global results are presented table 1 together with the few other measurements available in the litterature for the benzyl radical itself ; the rate constant of the benzyl radical with O_2 has already been measured by flash photolysis (16), laser photolysis/Laser Induced Fluorescence (17) and mass spectrometry (18). Our results for the substituted benzyl radicals show that the reaction rate with O_2 is not very dependent upon the presence of a substituent ; the same conclusion has been observed in liquid phase (19) for a few benzyl radicals substituted in para position by a methyl group or a fluorine atom. Furthermore, since the reaction rate constants with O_2 and NO measured with the present technique (Pressure $\sim$ 1 torr) are very close to those measured by flash photolysis ($\sim$160 torr) (16), this suggests that these reactions have already reached their high pressure limiting values ($k \propto$) at pressures in the torr range.

2) Variable temperature measurements

The rate constant with O_2 of the p-fluorobenzyl radical, considered as a model for the benzyl radical, has been measured in the range 297-433 K. Preliminary measurements indicate a strong negative temperature coefficient, in agreement with the following Arrhenius expression :

$$k = 4 \times 10^{-15} \exp(1590/T)\ cm^3\ molec^{-1}\ s^{-1}$$

This expression disagrees with the absence of any variation observed by Laser photolysis/Laser Induced Fluorescence (17) in the range 295-373 K ; however, it is in agreement with the lack of reactivity of benzyl with O_2 noticed by Troe et al (20) in their shock tube investigations ; furthermore, a few negative temperature coefficients have also been reported for the following ($R^\circ + O_2$ ---> products) reaction rates : R° = neopentyl (21), R° = ethyl (at constant [M]) (22), R° = i - C_4H_3 (23).

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Radical	Reactant			Ref
	O_2	NO	NO_2	
benzyl	0.99 1.5 > 0.5	9.5		(16) (17) (18)
p-fluorobenzyl	0.82	10	49	this work
m-fluorobenzyl	0.6	9	48	this work
o-methylbenzyl	1.2	9.4	50	this work
o-methylbenzyl	1.2	8.6		(16)
m-methylbenzyl	1.1	13	60	this work

Table 1 : rate constants of benzyl and substituted benzyl radicals (in 10^{-12} cm^3 $molec^{-1}$ s^{-1})

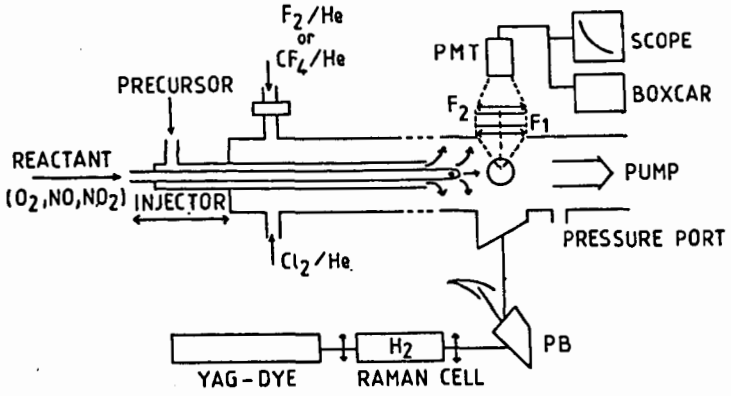

FIG.1
SCHEMATIC OF THE EXPERIMENTAL SET-UP

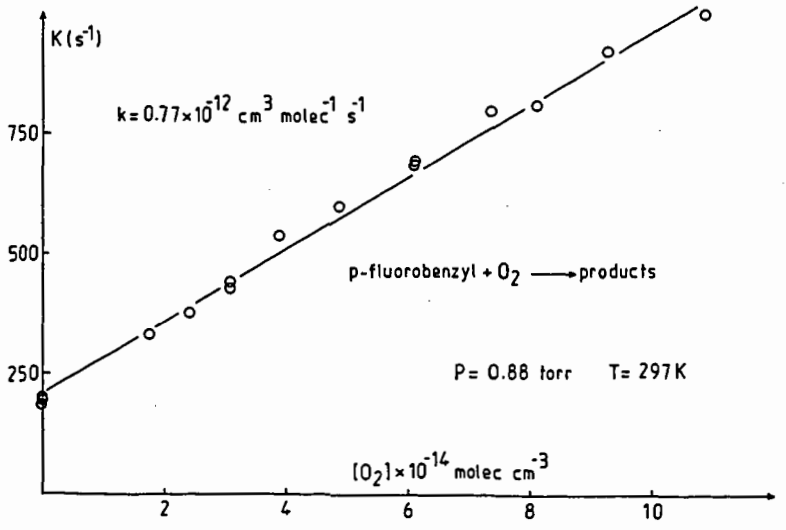

FIG.2b: PSEUDO-FIRST-ORDER RATE CONSTANTS ($K(s^{-1})$) VERSUS OXYGEN CONCENTRATION

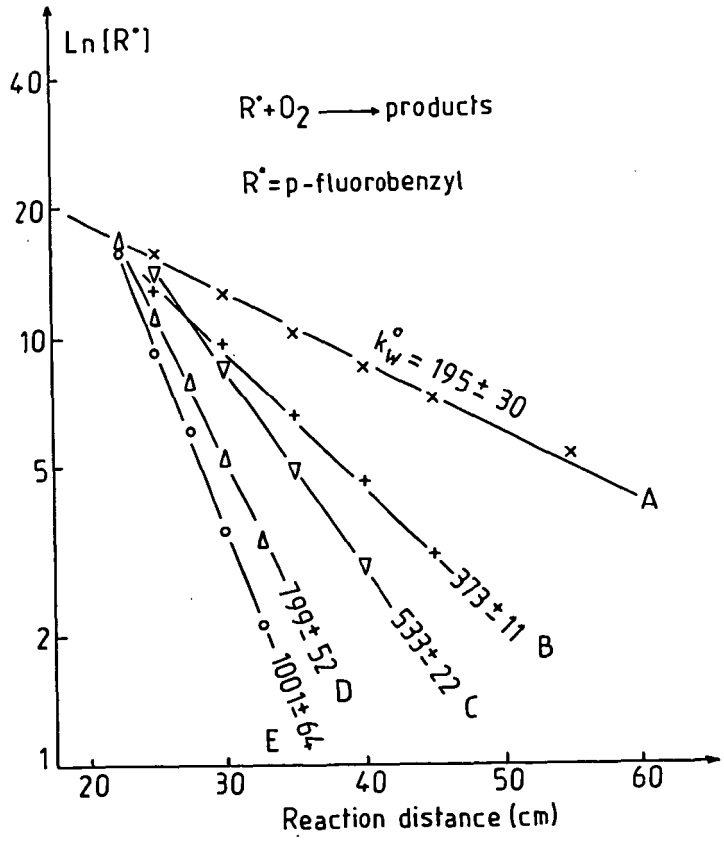

FIG 2a: RADICAL DECAY PLOTS VERSUS INJECTOR DISPLACEMENT (REACTION DISTANCE) FOR VARIOUS OXYGEN CONCENTRATONS (in 10^{*14} molec cm^{-3}): A(0), B(2.42), C(4.27), D(7.43) E(10.9); THE CORRESPONDING SLOPES ARE IN s^{-1}